Ion rotational distributions for nonlinear molecules at near-threshold photoelectron energies

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ABSTRACT

Rotationally resolved photoelectron spectra can provide significant insight into the underlying dynamics of molecular photoionization. Recent advances in experimental techniques now make it possible to readily achieve rotational resolution in molecular photoelectron spectra. Here we discuss results of our recent theoretical studies of rotationally resolved photoelectron spectra at near-threshold energies for the nonlinear molecules H_2O, H_2S, and CH_2O (formaldehyde). These studies serve to reveal the rich dynamics of molecular photoionization and, where possible, to provide a robust description of key spectral features of interest in related experimental studies.

1. INTRODUCTION

Rotationally resolved photoelectron spectra and their associated photoelectron angular distributions can clearly provide much insight into the dynamics of molecular photoionization, one of the simplest of molecular fragmentation processes. For example, these spectra are an obvious signature of the exchanges of energy and angular momentum between the photoelectron and molecular ion. Unfortunately, with the exception of hydrogen[1,2] and ionization from higher rotational levels of lighter systems such as NO (Ref. 3 and 4), OH (Ref. 5), and NH (Refs. 6 and 7), rotational resolution in photoelectron spectra has generally been beyond the reach of the techniques of conventional photoelectron spectroscopy. With the recent development of zero-kinetic-energy (ZEKE) photoelectron spectroscopy based on pulsed-field ionization (PFI) of very high Rydberg levels, however, it is now possible to exploit the narrow bandwidth of laser radiation to achieve sub-wave-number resolution in ion rovibronic state distributions.[8] The unprecedented resolution of this technique has led to a surge of experimental activity in molecular photoelectron spectroscopy.[9] The underlying dynamics of such threshold photoelectron spectra can be expected to be rich in content and to present new theoretical challenges.

Parity selection rules,[10-12] which govern the changes of rotational angular momentum, have been emphasized throughout studies of such spectra. For example, Tonkyn *et al.*[13] have observed type a rotational peaks, in addition to those of type c, in the threshold photoelectron spectra resulting from single-photon ionization of the $1b_1$ orbital of cooled H_2O by coherent VUV radiation. According to parity selection rules, these unexpected type a peaks arise from odd partial-wave contributions to the photoelectron matrix element which, in turn, are due to angular-momentum

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changing collisions of the photoelectron with the nonspherical molecular ion core.[11,12] Atomiclike propensity rules can clearly not account for such molecular behavior. One of the objectives of this article is to use such effects which arise from the molecular character of the photoelectron to highlight the underlying dynamics of rotationally resolved molecular photoionization. Examples chosen include ZEKE-PFI photoelectron spectra for single-photon ionization of the ground states of H_2O, H_2S and CH_2O (formaldehyde) by coherent VUV radiation.

An outline of the paper is as follows. In section 2, we briefly present the theory for rotationally resolved photoionization of nonlinear molecules. Parity selection rules, which govern the angular momentum transfer between the photoelectron and molecular ion core, are also discussed. In section 3, we present calculated rotationally resolved photoelectron spectra and compare these results with measured spectra for the molecules identified above.

2. THEORY

The general theory of molecular photoionization of nonlinear molecules used in the present studies is described elsewhere.[10–12] Here we present just a brief outline of some essential features of our procedure as it is used to obtain ion rotational distributions for single-photon ionization of nonlinear molecules. For linearly polarized light the differential photoionization cross section can be expressed in terms of Legendre polynomials as

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\Big[1 + \beta\ P_2(\cos\theta)\Big], \tag{1}$$

where σ is the total cross section, β the asymmetry parameter, $P_2(\cos\theta)$ the Legendre polynomial, and θ the angle between the direction of the photoelectron and the electric vector of the polarized light. Under collision-free conditions, ionization originating from each of the $(2J_0 + 1)$ magnetic sublevels of the initial state forms an independent channel. Therefore, the total cross section σ and asymmetry parameter β for ionization of a J level of the ground state can be written, respectively, as[10]

$$\sigma \propto \sum_{\substack{\ell m \\ M_J, M_{J+}}} \rho_{M_J M_J} |C_{\ell m}(M_J M_{J+})|^2, \tag{2}$$

and

$$\beta = \frac{5}{\sigma} \sum_{\substack{\ell \ell' m \\ M_J, M_{J+}}} (-1)^m (2\ell + 1)(2\ell' + 1)\rho_{M_J M_J} C_{\ell m}(M_J M_{J+}) C^*_{\ell' m}(M_J M_{J+}) \begin{pmatrix} \ell & \ell' & 2 \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} \ell & \ell' & 2 \\ 0 & 0 & 0 \end{pmatrix}, \tag{3}$$

where $\rho_{M_J M_J}$ is the population of an unaligned M_J level of the ground state. The coefficients $C_{\ell m}(M_J M_{J+})$ of Eqs. (2) and (3) are related to the probability for photoionization of the M_J

level of the ground state leading to the M_{J+} level of the ion. An expression for $C_{\ell m}(M_J M_{J+})$ has been given by Lee *et al.*[10] for asymmetric top molecules by explicitly considering the spin coupling associated with multiplet-specific final-state wave functions and Hund's case (b) for the ground and ionic states. For the branching ratios of interest here, the constant implied in Eq. (2) is unimportant and will be suppressed.

A central quantity in these studies is the matrix element for photoejection of an electron from a bound molecular orbital ϕ_i into a photoelectron continuum orbital $\Psi^{(-)}_{f,\mathbf{k}}(\mathbf{r})$. Here $\mathbf{k}$ is the momentum of the photoelectron and $(-)$ denotes incoming-wave boundary conditions. For asymmetric top molecules, the partial wave components $\psi^{(-)\gamma q}_{kh\ell m}$ of $\Psi^{(-)}_{f,\mathbf{k}}(\mathbf{r})$ are defined by an expansion in generalized harmonics about $\hat{\mathbf{k}}$ of the photoelectron

$$\Psi^{(-)}_{f,\mathbf{k}}(\mathbf{r}) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \sum_{\ell m} i^{\ell}\ \psi^{(-)\gamma q}_{kh\ell m}(\mathbf{r}) X^{*\gamma q}_{h\ell m}(\hat{\mathbf{k}}), \tag{4}$$

where $X^{\gamma q}_{h\ell m}(\hat{\mathbf{k}})$ is a generalized harmonic, γ is one of the irreducible representations (IR) of the molecular point group, q is a component of this representation, and h distinguishes between different bases for the same IR corresponding to the same value of ℓ. Single-center expansions of $\psi^{(-)\gamma q}_{kh\ell m}(\mathbf{r})$ and $\phi^{\gamma' q'}_i(\mathbf{r}')$, e.g.,

$$\psi^{(-)\gamma q}_{kh\ell m} = \sum_{\ell' \lambda} g^{\gamma q}_{h\ell m,\ell' \lambda}(k,r) \mathcal{D}^{\ell'}_{m\lambda} X^{\gamma q}_{h\ell' \lambda}(\hat{\mathbf{r}}'), \tag{5}$$

define partial-wave photoelectron matrix elements $r^{\gamma q}_{h\ell\lambda\mu}(R)$ in the molecular frame for ionization out of orbital $\phi^{\gamma' q'}_i(\mathbf{r}')$, i.e.,[10]

$$r^{\gamma q}_{h\ell\lambda\mu}(R) = \sum_{\ell', \ell_o} \langle g^{\gamma q}_{h\ell m,\ell' \lambda}(k,r,R) X^{\gamma q}_{h\ell' \lambda}(\hat{\mathbf{r}}') | r\ Y_{1\mu}(\hat{\mathbf{r}}') | \phi^{\gamma' q'}_{ih'\ell_0}(r,R) X^{\gamma' q'}_{h'\ell_0,\lambda_0}(\hat{\mathbf{r}}') \rangle, \tag{6}$$

where R denotes a dependence on internuclear distance, μ the photon polarization index in the molecular frame, m and λ the projection of ℓ in the laboratory and molecular frames, respectively, and $\mathcal{D}^{\ell}_{m\lambda}$ a rotational matrix in Edmonds's notation.[14]

Equation (6) reveals an important underlying dynamical aspect of molecular photoelectron wave functions. Whereas only $\ell = \ell'$ terms are allowed in Eq. (6) for the central fields of atomic systems, where the angular momentum of the photoelectron must be conserved, $\ell \neq \ell'$ terms arise in Eq. (6) due to the nonspherical potential fields of molecular ions. This angular momentum coupling between partial waves ℓ and ℓ' is brought about by the torques associated with the molecular ion potential and makes a molecular photoelectron orbital an admixture of angular momentum components. Viewed very simply, this means that whatever angular momentum ℓ a photoelectron may have at a given instant can be changed as the photoelectron scatters off the molecular ion. Furthermore, for the nonlinear molecules of interest here, projections of angular

momenta may also be changed by these nonspherical ion-core potentials and terms with $m \neq \lambda$ arise in Eq. (6).[11,12] These angular-momentum changing collisions between the photoelectron and molecular ion play a crucial role in rotationally resolved molecular photoelectron spectra. The use of molecular photoelectron orbitals which correctly incorporate such angular momentum coupling is essential at the low photoelectron energies of interest here.

Parity selection rules,[10–12] governing changes of rotational angular momentum upon ionization, have been derived previously for nonlinear molecules. For asymmetric top molecules, the parity selection rules are modified to govern the changes of angular momenta ΔK_a and ΔK_c where $\Delta K_a = K_{a+} - K_a$ and $\Delta K_c = K_{c+} - K_c$ and K_a and K_c are the projections of total angular momentum (except spin) along the principal a and c axes, respectively. With a choice of a left-handed coordinate system for the molecule-fixed x, y, and z axes and choosing the molecular z axis to be the symmetry axis, Lee *et al.*[10] have derived the selection rules

$$\Delta K_\eta + \ell = odd, \tag{7}$$

and

$$\mu + \lambda = \begin{cases} \Delta K_a, & \text{if } a//z// \text{ the symmetry axis} \\ \Delta K_b, & \text{if } b//z// \text{ the symmetry axis} \\ \Delta K_c, & \text{if } c//z// \text{ the symmetry axis} \end{cases}, \tag{8}$$

where η is the principal axis which lies along the molecular x axis and K_η the projection of the total angular momentum along this axis. To make use of the selection rules of Eqs. (7) and (8), a relationship among ΔK_a, ΔK_b, and ΔK_c is also needed, i.e.,

$$\Delta K_a + \Delta K_c = even(odd) \leftrightarrow \Delta K_b = even(odd), \tag{9}$$

Equation (9) is based on the symmetry properties of the asymmetric top.[15] Clearly, the determination of $\mu + \lambda$ becomes a crucial step in application of these selection rules. Although Eqs. (7–9) are suitable for any nonlinear polyatomic molecule, $\mu + \lambda$ has to be determined specifically for a given symmetry. These selection rules will be further illustrated in later sections of this paper.

In applications of our procedure to single-photon ionization of the ground state of molecules, we use a self-consistent-field (SCF) Hartree-Fock wave function to represent the initial state. For the final state we assume a frozen-core Hartree-Fock model in which the core orbitals are taken to be those of the ion with the unrelaxed orbitals of the neutral ground state and the photoelectron orbital is obtained as a solution of a one-electron Schrödinger equation containing the Hartree-Fock potential of this molecular ion, $V_{ion}(\mathbf{r}, R)$, i.e.,

$$\left(-\frac{1}{2}\nabla^2 + V_{ion}(\mathbf{r}, R) - \frac{k^2}{2}\right) \psi^{(-)\gamma q}_{kh\ell m}(\mathbf{r}, R) = 0. \tag{10}$$

To obtain the partial wave photoelectron orbitals $\psi^{(-)\gamma q}_{kh\ell m}$, we use an iterative procedure, based on the Schwinger variational principle, to solve the Lippmann-Schwinger equation associated with

Eq. (10).[16] A few iterations of this iterative variational method provide highly converged solutions for these molecular photoelectron orbitals. In studies of rotationally resolved photoelectron spectra at low photoelectron energies, e.g., as small as 0.05 eV, it is essential to use such converged solutions so as to faithfully represent the angular momentum coupling present in the molecular photoelectron wave function. Further details of calculations can be found in Refs. 11 and 12 for H_2O, Ref. 17 for H_2S, and Ref. 18 for CH_2O.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the rotationally resolved ZEKE-PFI spectrum of H_2O recently reported by Tonkyn *et al.*[13] for single-photon ionization of the $1b_1$ orbital by coherent VUV radiation. This spectrum can be assigned to two types of rotational transitions, corresponding to specific changes in K_a and K_c. Most of the strong spectral lines could be classified as type c rotational transitions ($\Delta K_a = odd$, $\Delta K_c = even$), but type a transitions ($\Delta K_a = even$, $\Delta K_c = odd$) are also clearly evident. Figure 8(b) shows the calculated ion rotational distributions of Lee *et al.*[11,12] for photoionization of the $1b_1$ orbital of the $\tilde{X}\ ^1A_1$ (000) ground state of jet-cooled H_2O leading to the $\tilde{X}\ ^2B_1$ (000) ground state of the ion. A photoelectron kinetic energy of 50 meV and a rotational temperature of 15 K are assumed in these calculations. Furthermore, we assume that there is no spin exchange taking place during the jet-cooled expansion of room-temperature water. The calculated spectrum is convoluted with a Gaussian detection function with a full-width at half-maximum (FWHM) of 1.5 cm^{-1}. The agreement between the calculated and measured spectra is clearly encouraging except for the calculated $0_{00} \rightarrow 2_{12}$ transition which is somewhat stronger than that of measured value.

The underlying dynamics of these photoelectron spectra is quite rich. From the parity selection rules of Eqs. (7) and (8), we obtain[11,12]

$$\Delta K_a + \ell = odd, \tag{11}$$

and

$$\mu + \lambda = \Delta K_b. \tag{12}$$

Here we assume that the molecular z axis coincides with the C_2 symmetry axis and the x axis lies in the plane of the molecule (ion). The molecular x, y, and z axes hence coincide with the a, c, and b axes, respectively. For photoionization of the $1b_1$ orbital of H_2O, $\mu + \lambda$ is always odd and, hence, from Eq. (9) we have

$$\Delta K_a + \Delta K_c = odd. \tag{13}$$

Clearly, both type a and type c transitions are allowed and type b [$\Delta K_a = even(odd)$ and $\Delta K_c = even(odd)$] transitions are forbidden. Furthermore, Eq. (11) shows that type a transitions ($1_{01} \rightarrow 0_{00}$, $0_{00} \rightarrow 1_{01}$, $1_{01} \rightarrow 2_{02}$, and $1_{11} \rightarrow 2_{12}$) arise from odd (almost pure p) wave contributions to the photoelectron matrix element of Eq. (6). These p waves of the ka_1

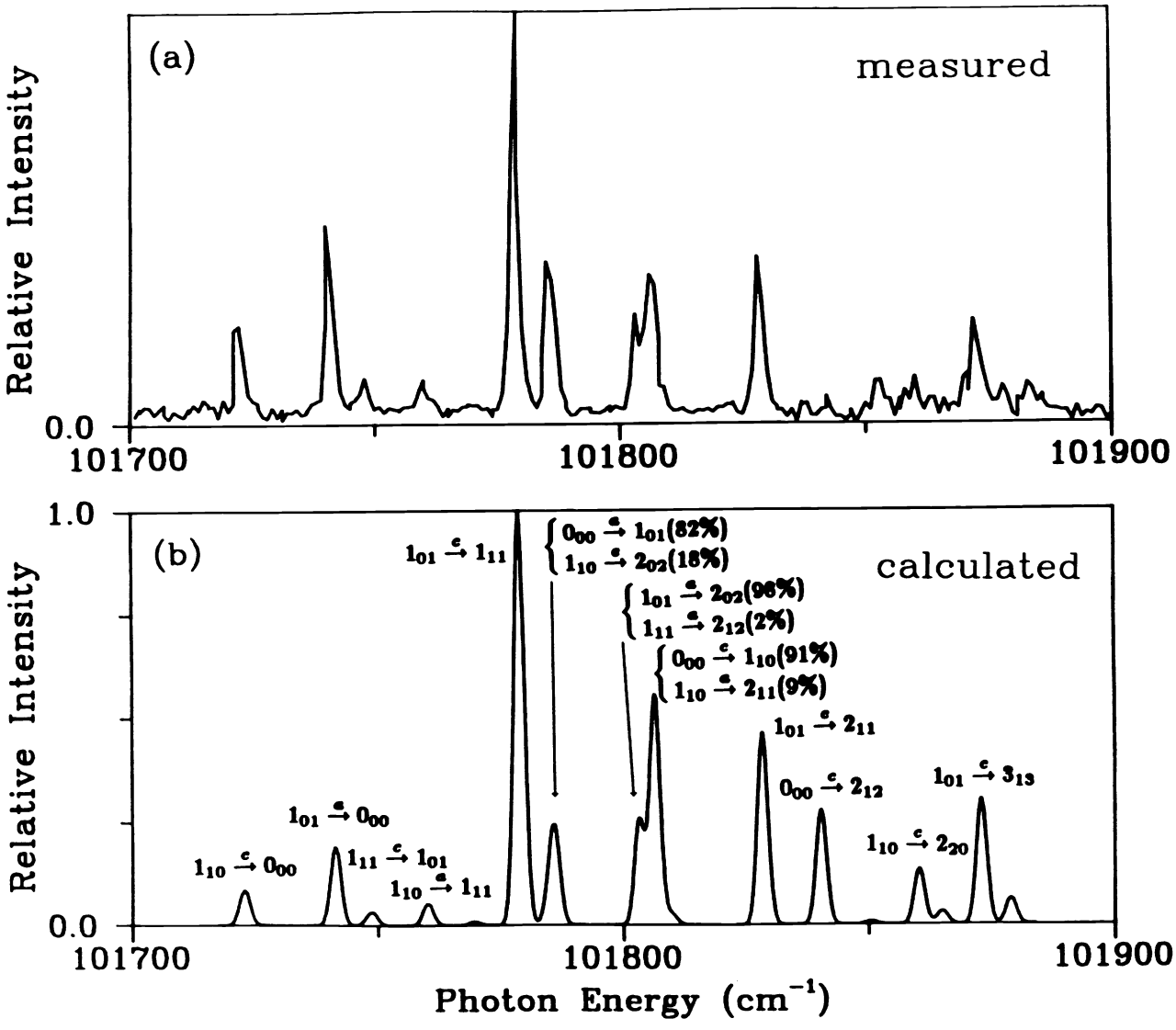

Fig. 1. (a) measured and (b) calculated ion rotational distributions for single-photon ionization of the $1b_1$ orbital of the $\widetilde{X}\ ^1A_1$ ground state of jet-cooled H_2O. The a and c labels indicate type a and type c transitions, respectively.

and kb_1 continua are entirely molecular in origin, since the almost pure p (99.7 %) character of the $1b_1$ orbital leads only to s and d (even) photoelectron continua in an atomiclike picture. The strong type c transitions in these spectra arise from s and d (even) wave components of the photoelectron matrix element. The ka_2 continuum makes almost no contribution to these type a transitions since the f (odd) wave is negligible. In a recent study using multichannel quantum defect theory (MQDT), Child and Jungen[19] predicted that only type c transitions are allowed for photoionization of the $1b_1$ orbital of ground state water. Gilbert and Child[20] further proposed a rotational autoionization mechanism, based on polarization-induced quasiautoionizing state-

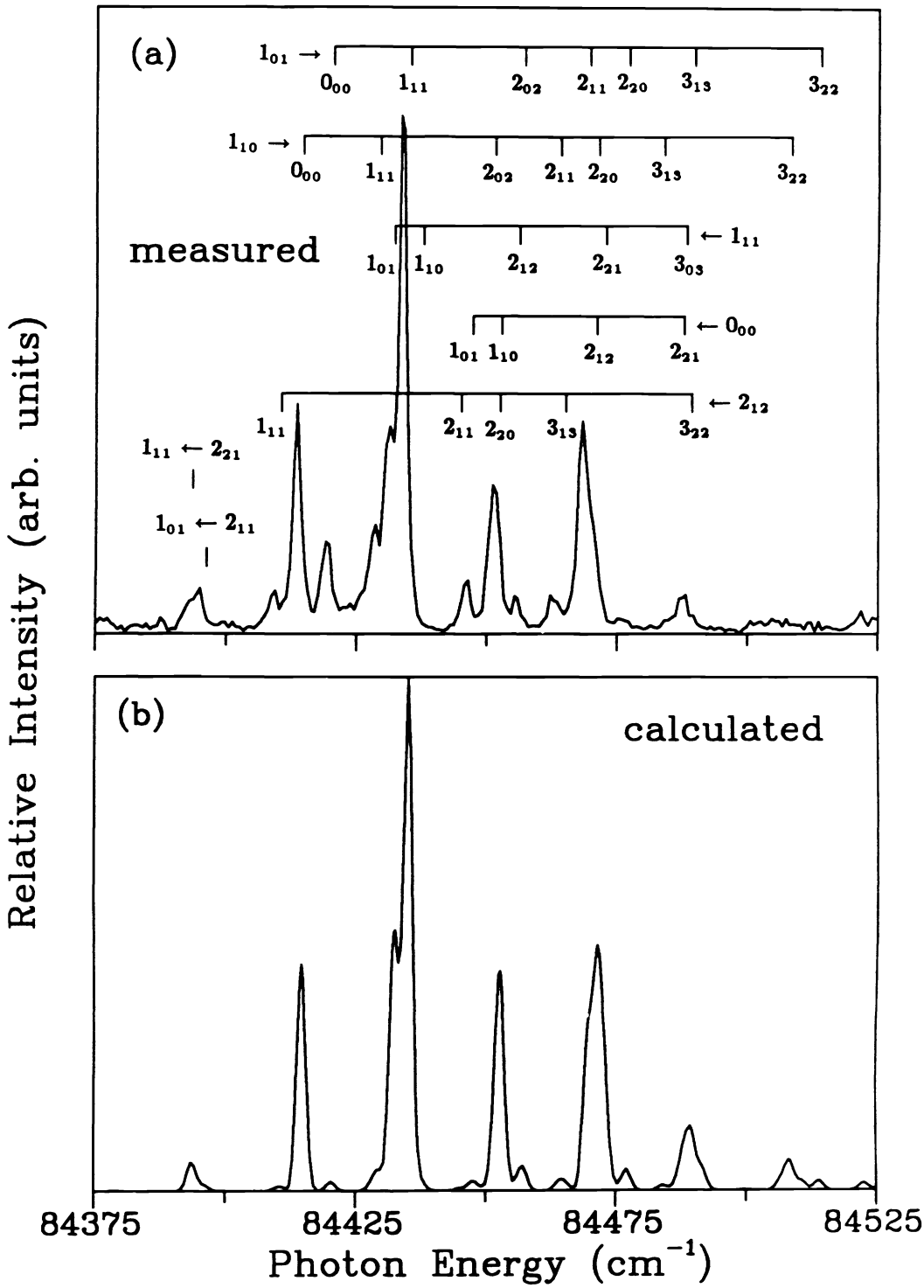

Fig. 2. (a) measured and (b) calculated ion rotational distributions for single-photon ionization of the $2b_1$ orbital of the $\tilde{X}\ ^1A_1$ ground state of jet-cooled H_2S. The calculated spectrum is for 20 K and has an FWHM of 2 cm^{-1}.

mixing between the $1b_1 \rightarrow nd$ and $1b_1 \rightarrow np$ Rydberg series, in an effort to account for these type a transitions. In contrast, the above analysis[11,12] shows that these type a transitions arise quite naturally in a correct quantitative description of the direct molecular photoionization process itself and a polarization-induced autoionization mechanism need not be invoked.

Figure 2 shows the (a) measured[17,21] and (b) calculated ion rotational distributions for single-photon ionization of the $2b_1$ orbital of the $\widetilde{X}\ ^1A_1$ (000) ground state of jet-cooled H_2S by coherent VUV radiation leading to the $\widetilde{X}\ ^2B_1$ (000) ground state of the ion. A rotational temperature of 20 K is assumed in these calculations. These ion spectra are similar to those for the (000) level of H_2O^+ of Fig. 1 in that threshold photoionization is accompanied by only small changes in total angular momentum (excluding spin) ΔN and both type c ($\Delta K_a = \pm 1$, $\Delta K_c = 0$) and type a ($\Delta K_a = 0$, $\Delta K_c = \pm 1$)transitions are observed. The photoionization dynamics of the $2b_1$ orbital of H_2S can be expected to be very similar to that of the $1b_1$ orbital of H_2O since the $2b_1$ orbital is primarily localized on the sulfur atom and has about 99.8 %p character. Furthermore, type a transitions can also be expected to be weaker relative to type c transitions in the photoelectron spectra of H_2S than in H_2O due to the more atomiclike character of H_2S. In fact, a type c to type a intensity ratio of 4:1 is seen for photoionization of H_2S in contrast to a 2:1 ratio for H_2O. The agreement between the calculated and measured spectra is very encouraging even though the type a transition ($1_{01} \rightarrow 0_{00}$) with negative ΔN is somewhat weaker in the calculated spectrum than observed. However, the $1_{01} \rightarrow 2_{02}$ type a transition with $\Delta N = 1$ has almost the same intensity as seen in the measured spectrum. The same photoelectron matrix elements are used in the calculation of the spectral intensities of these two type a transitions. This strongly suggests that the type a transition with negative ΔN is not due exclusively to direct ionization but probably involves rotational autoionization.[22–25] A field-induced autoionization mechanism involving the interaction of high-n Rydberg states ($n > 150$) with lower-n levels ($20 < n < 80$) converging to higher rotational state thresholds of the cation has successfully accounted for this behavior.[23] This behavior is also observed in the threshold photoionization spectra of OH (Ref. 22), N_2O (Ref. 23), and HCl (Ref. 24 and 25) and in several (1+1′) resonance enhanced multiphoton ionization ZEKE photoelectron spectra for single rotational levels of the $A\ ^2\Sigma^+$ ($3s\sigma$) Rydberg state of NO (Refs. 26–28). Such comparisons between measured spectra and spectra calculated on the basis of direct ionization can clearly be helpful in clarifying the role of autoionization in these threshold photoelectron spectra.

Figure 3 shows the (a) measured[18] and (b) calculated rotationally resolved ZEKE-PFI spectra of CH_2O for single-photon ionization of the nonbonding $2b_2$ orbital by coherent VUV radiation. The calculated spectrum assumes a rotational temperature of 7 K and a photoelectron kinetic energy of 50 meV and is convoluted with a Gaussian detection function with an FWHM of 1.8 cm^{-1}. Furthermore, we assume that there is no spin exchange taking place during the jet-cooled expansion of room-temperature formaldehyde, i.e., a population ratio of 2:1 is kept for the ortho (B symmetry) to para (A symmetry) species. The agreement between calculated and measured spectra is very encouraging.

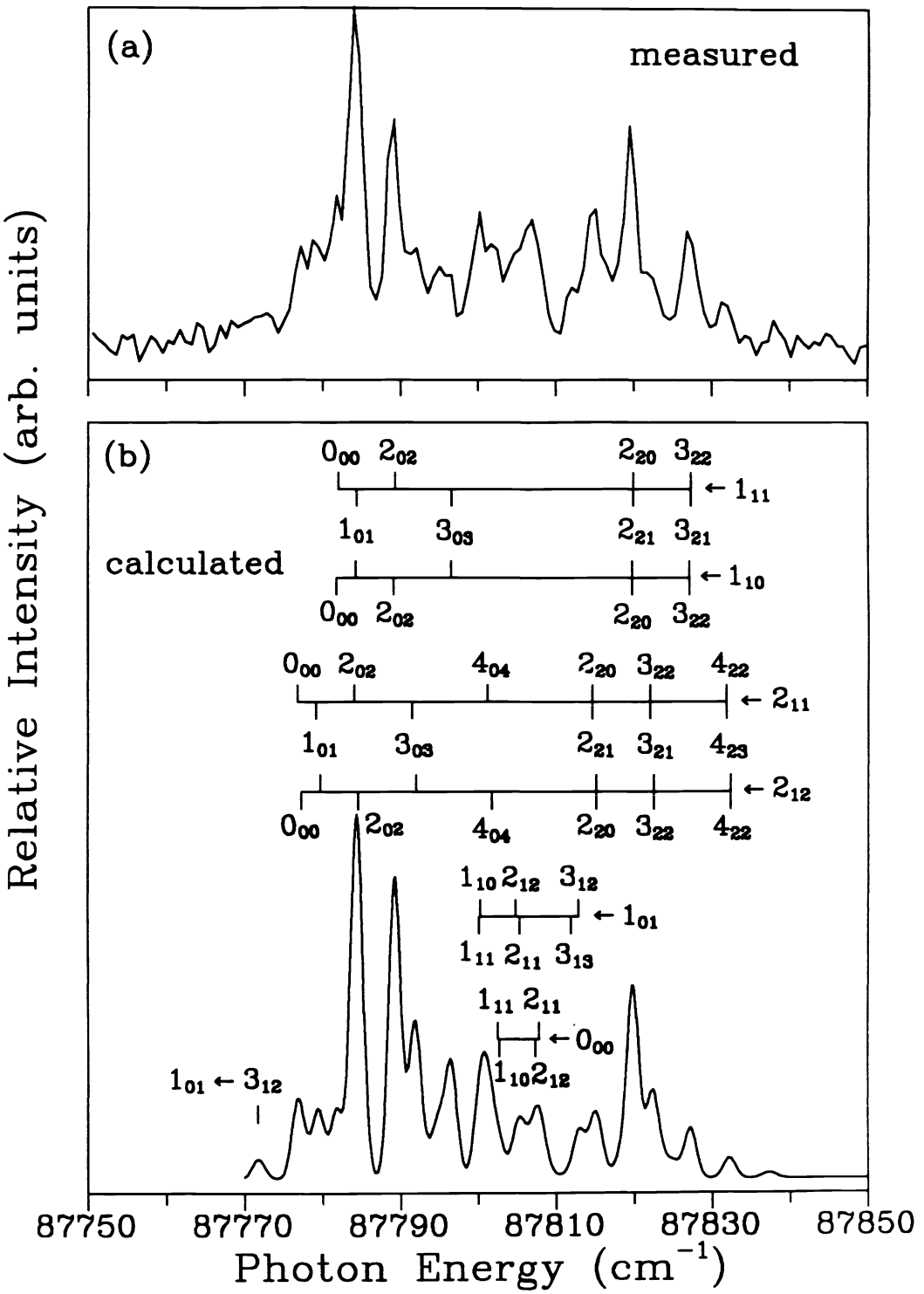

Fig. 3. (a) measured and (b) calculated ion rotational distributions for single-photon ionization of the $2b_2$ orbital of the $\tilde{X}\ ^1A_1$ ground state of jet-cooled CH_2O. The calculated spectrum is for 7 K and has an FWHM of 1.8 cm^{-1}.

In our calculations we assume that the molecular z axis coincides with the C_2 symmetry axis and the x axis lies in the plane of the formaldehyde molecule (ion). The molecular x, y, and z axes hence coincide with the b, c, and a axes, respectively. From the parity selection rules of Eqs. (7) and (8), we obtain[11,12]

$$\Delta K_b + \ell = odd, \tag{14}$$

and

$$\mu + \lambda = \Delta K_a. \tag{15}$$

For photoionization of the $2b_2$ orbital of CH_2O, $\mu + \lambda$ is always odd and, hence, from Eq. (9) we have

$$\Delta K_b + \Delta K_c = odd. \tag{16}$$

Clearly, both type c ($\Delta K_a = odd$ and $\Delta K_c = even$) and type b ($\Delta K_a = odd$ and $\Delta K_c = odd$) transitions are allowed and type a ($\Delta K_a = even$ and $\Delta K_c = odd$) and other type b ($\Delta K_a = even$ and $\Delta K_c = even$) transitions are forbidden. Furthermore, Eqs. (14–16) show that the allowed type b transitions arise from odd partial wave contributions to the photoelectron matrix element of Eq. (6) whereas the type c transitions arise from even angular momentum components of the photoelectron.

In Fig. 3(b), we label several of the more important transitions out of rotational levels of the ground state of the neutral species leading to different rotational levels of the ion. The quantum numbers used as labels are $N_{K_a K_c}$. Note that in this figure we use the same set of quantum numbers to designate type c transitions out of the 1_{11} level and type b transitions out of the 1_{10} level, since the energies of these transitions are essentially equal. A similar labeling is also adopted for transitions out of the 2_{11} and 2_{12} rotational levels. The calculated intensities for several dominant transitions are given elsewhere.[18] Since the moment of inertias I_b and I_c are almost the same for CH_2O (CH_2O^+), the rotationally resolved ZEKE-PFI spectra are very congested. Unlike the spectra for H_2O and H_2S, type b transitions, which arise from odd waves, cannot be distinguished from type c transitions, which arise from even waves. However, our calculated spectrum shows a total intensity for type b transitions about 1.9 times larger than that for type c transitions. This large intensity of the type c transitions cannot be accounted for on the basis of atomiclike propensity rules since the $2b_2$ orbital of the CH_2O has 4.8 % p, 80.0 % d, 3.7 % f, 9.1 % g ($\ell_0 = 4$), and 1.5 % h ($\ell_0 = 5$) character. The strong even-wave character of the $2b_2$ orbital would be expected to lead to dominant odd partial wave contributions to the photoelectron matrix elements and, hence, to dominant type b transitions. This unexpected contribution from even partial waves of the photoelectron matrix element is quite molecular in origin and arises from strong ℓ-mixing due to the nonspherical molecular ion potential. Note that a shape resonance is predicted in the ka_1 photoelectron continuum at kinetic energies of about 5 eV.[29] However, this shape resonance should have very little effect on the threshold photoionization ZEKE-PFI spectrum. Such comparisons between measured and calculated spectra can be helpful in unravelling severely congested photoelectron spectra.

4. ACKNOWLEDGMENTS

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